

# Piezoelectric and Dielectric Characteristics of Single-Crystal Barium Titanate Plates

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*The dielectric constant of c-domain barium titanate single-crystal plates has been measured as a function of their average polarization, using ac voltages much smaller than the coercive voltage. As has been found previously, the dielectric constant at frequencies below thickness fundamental resonance has a minimum at zero average polarization. However, at frequencies well above thickness resonance the dielectric constant has a maximum at zero polarization. The variation is about 25 per cent from minimum to maximum in both frequency ranges. In both frequency ranges the conductance is highest at zero polarization.*

*The piezoelectric output voltage of a BaTiO<sub>3</sub> single crystal subjected to a recurrent strain pulse of constant amplitude has been found to be approximately, but not exactly, proportional to its average polarization. There appears, in fact, to be a distinct hysteresis in the dependence.*

## I. INTRODUCTION

The physical properties of BaTiO<sub>3</sub> have been investigated extensively in the last few years, and the ferroelectric characteristics of single crystals have found several applications in electrical circuit devices. On the other hand, applications of the piezoelectric characteristics of BaTiO<sub>3</sub> have largely been limited to its ceramic form. The experiments reported in this paper were initially undertaken to investigate the possible usefulness of the piezoelectric characteristics of BaTiO<sub>3</sub> single crystals in practical devices.

In the work reported in this paper, dielectric and piezoelectric characteristics of BaTiO<sub>3</sub> in single crystals were investigated by means of two types of electrical measurements. A crystal plate with electrodes is essentially a two-terminal circuit element. The admittance of crystals as passive elements has been measured as a function of average remanent

polarization above, below and in the vicinity of the fundamental resonant frequency in the thickness-extensional mode. When such a crystal is excited by ultrasonic radiation it becomes a voltage source. The output voltage of an ultrasonically excited crystal has been observed as a function of average remanent polarization when the ultrasonic excitation was at frequencies in the vicinity of the fundamental resonant frequency in the thickness-extensional mode.

Certain features of the piezoelectric behavior of  $\text{BaTiO}_3$  single crystals have been measured before by Bond, Mason and McSkimin,<sup>1</sup> by Caspari and Merz,<sup>2</sup> by Drougard and Young<sup>3</sup> and by Huibregtse, Drougard and Young.<sup>4</sup> Measurements having particular bearing on the work reported in this paper were made by Drougard and Young, who measured the low-frequency, small-signal capacitance of  $\text{BaTiO}_3$  crystals as a function of their average polarization. This type of measurement receives further elaboration in the present paper.

When comparing reported results of measurements of dielectric and other material constants, one should bear in mind that the quality of  $\text{BaTiO}_3$  single crystals may vary considerably. The dielectric constant is a rather good index of the fraction of *a*-domains in these crystals because it is much higher for *a*-domains than for *c*-domains. The low-frequency dielectric constant ( $K_{33}^T$ ) was earlier reported to have values ranging from 185 to approximately 3000. These values should be compared with later values found by Merz<sup>5</sup> of 160 and our own values, which are in this same range.

For applications of the type we wished to consider, plate-shaped, *c*-domain crystals were most suitable. Plate-shaped crystals were grown by the method of Remeika<sup>6</sup> and were rendered entirely *c*-domain by application of an electric field perpendicular to the plate. Coin silver electrodes  $\frac{3}{16}$  inch in diameter and about 1000 Å thick were evaporated onto the broad sides of the plate.

Some crystals were bonded with Araldite to fused silica rods before being measured. The operations of electroding and bonding, where they occurred, could possibly have introduced *a*-domains, but these could not be detected by polarized light because both the electrodes and the silvered surfaces of the fused silica were opaque. However, the low values of dielectric constant lead us to believe that the plates were very nearly pure *c*-domain during our measurements.

In the course of the experiments to be reported, measurements were made on several dozen  $\text{BaTiO}_3$  single crystals having different thicknesses and electrode configurations. From the reader's point of view it would be simplest if all the different types of measurements reported were reported

on the same crystal. This was not practical, but the number of samples has been limited to three crystals, which have been designated as crystals "A", "B" and "C". For these crystals, certain quantities were measured as functions of polarization, and a complete set of numerical results for dielectric and piezoelectric quantities is presented in Table I (see page 731). All the crystals observed, including the three selected crystals, exhibited variations in behavior, due perhaps to undetected differences in processing. For measurements where the results varied considerably from crystal to crystal, the variations will be specifically mentioned.

## II. EXPERIMENTAL METHODS AND RESULTS

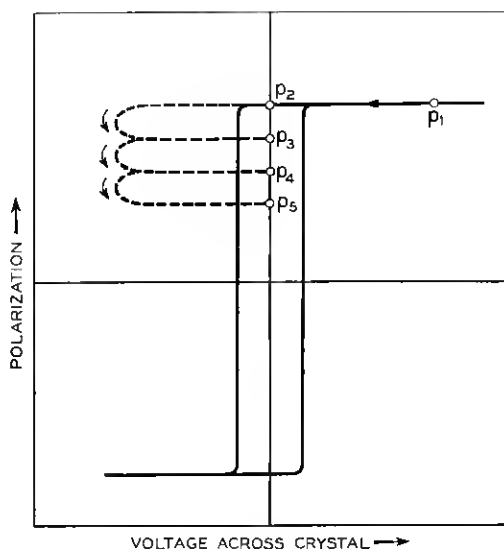
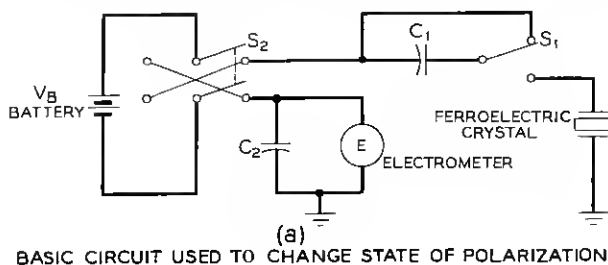
### 2.1 *Method of Varying Average Polarization*

The average polarization of a  $\text{BaTiO}_3$  crystal was changed by means of the circuit shown in Fig. 1(a).<sup>7</sup> The value of  $C_1$  was chosen so that a small amount of charge,  $C_1 V_B$ , could be moved through the crystal each time the switch  $S_1$  was moved from the shorting position to the position connecting the capacitor in series with the crystal;  $C_1$  was chosen so that  $C_1 V_B$  was approximately  $\frac{1}{35} Q_r$ , where  $Q_r$  is the remanent charge. For the crystals used in these experiments,  $Q_r$  was approximately 5 microcoulombs,  $C_1$  was 0.002 microfarads and  $V_B$  was 67 volts. The changes in the crystal's state of polarization produced by the circuit of Fig. 1(a) may be interpreted in terms of the diagram shown in Fig. 1(b). The crystal may be put in the state of polarization indicated by the point  $p_1$  on the loop by applying a voltage which is greater than the coercive voltage. When the crystal is shorted, it changes to position  $p_2$  on the hysteresis loop. When an amount of charge equal to  $C_1 V_B$  has passed through the series circuit all the voltage appears across  $C_1$  and the crystal is now in position  $p_3$ . The charge accumulated on  $C_1$  can be shorted out by  $S_1$  and the switching process can be repeated until the polarization saturates in the opposite direction. Reversing the applied voltage will return the crystal, a step at a time, to position  $p_2$ . For some observations, the crystal was also switched slowly and continuously by the use of a large resistance (of the order of  $10^{10}$  ohms) in place of  $C_1$ . In either case, the charge moved through the crystal was measured by the electrometer  $E$  across the low-leakage capacitor  $C_2$ .

### 2.2 *Admittance Measurements*

In general, the admittance of a dielectric material between two electrodes is a complicated function of frequency, depending upon the pres-

ence of various types of physical phenomena such as piezoelectricity, ferroelectricity, relaxation effects or electrostriction. In the case of a given sample of material, measurements of admittance over a wide range in frequency are used to establish which physical phenomena are present. In addition to having a dependence upon frequency, values of admittance are frequently dependent upon the current level at which the measurements were made. This is true for  $\text{BaTiO}_3$  single crystals, which have the added complication that the admittance at a particular frequency de-



(b)

AN IDEALIZED HYSTERESIS LOOP OF A FERROELECTRIC CRYSTAL AND THE PATH FOLLOWED IN CHANGING THE STATE OF POLARIZATION

Fig. 1 — (a) Circuit for switching small amounts of charge through a ferroelectric crystal; (b) diagram of crystal's hysteresis loop showing path traced by circuit of (a).

depends upon the state of polarization. It is possible (and desirable for many applications) to switch a crystal to an arbitrary polarization by means of the type of circuit shown in Fig. 1(a). Admittance may then be measured as a function of frequency for that particular value of average polarization. Provided that the measuring circuit does not place across the crystal a voltage large enough to move domains, the crystal will stay at the set value of average polarization.

All the admittance measurements reported in this paper were made with measuring voltages across the crystal small enough so that the polarization of the crystal was left unchanged by a measurement. With this sort of technique we could, therefore, measure admittance at a given frequency as a function of polarization or measure admittance at a given polarization as a function of frequency.

*2.2.1 Admittance Measurements in the Vicinity of the Fundamental Resonant Frequency of the Thickness-Extensional Mode.* The admittance of a dielectric material having piezoelectric characteristics varies greatly with frequency when it is near resonance, compared with the frequency dependence of the admittance far removed from a resonant frequency. For this reason, admittance measurements fall rather naturally into two major types: (1) those near resonance and (2) those far removed from resonance.

In order to define several terms of which we will make frequent use, we show in Fig. 2 the admittance characteristics of a simple piezoelectric resonator having a frequency dependence of admittance that closely approximates the behavior of our  $\text{BaTiO}_3$  crystals at maximum polarization. In this figure the admittance of the resonator at any frequency,  $f$ , is given in terms of its capacitance,  $C_E(f)$ , and its shunt resistance  $R_E(f)$  according to

$$Y(f) = \frac{1}{R_E(f)} + j\omega C_E(f). \quad (1)$$

The series resonant frequency,  $f_s$ , is defined as that frequency at which  $R_E(f)$  is a minimum. Two other characteristic frequencies are  $f_r$ , the resonant frequency, and  $f_a$ , the antiresonant frequency. At  $f_r$ ,  $C_E(f)$  equals zero and  $dC_E/df$  is negative; at  $f_a$ ,  $C_E(f)$  is again zero and  $dC_E/df$  is positive.

The resonant and antiresonant frequencies in the thickness-extensional mode of the  $\text{BaTiO}_3$  crystals described above were measured by an admittance bridge technique described elsewhere.<sup>8</sup> After the average polarization was set by the circuit of Fig. 1(a), the crystal was removed to the admittance bridge for measurement. The value of the polarization,

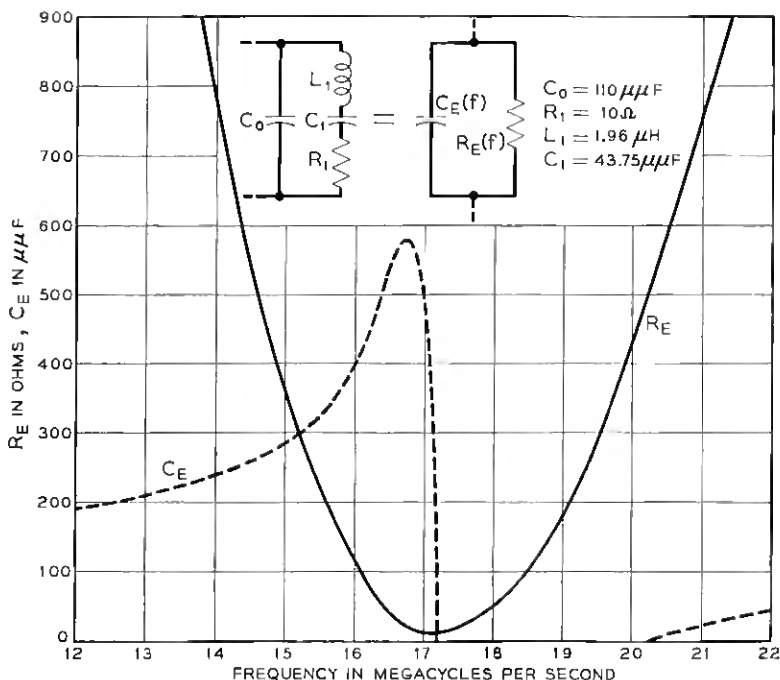


Fig. 2 — Admittance characteristics of a simple piezoelectric crystal near its resonant frequency.

measured by the electrometer, was found to be unchanged after the admittance measurement.

The admittance of an unbonded crystal was measured as a function of frequency, both in a state of maximum polarization and in a state of nearly zero polarization. The capacitance and shunt resistance are plotted against frequency in Fig. 3 for maximum polarization and in Fig. 4 for nearly zero average polarization. The many small erratic variations in the curves of Fig. 3, as compared with those of Fig. 2, are attributed to the presence of multiple resonances possibly due to the uneven surfaces\* of the crystal plate. Fig. 5 shows a plot of resonant and anti-resonant frequencies of the same crystal as a function of polarization.

Measurements exactly the same as those made on unbonded crystals were made on a similar crystal which had been bonded with Araldite

\* The surfaces of the crystal plates were not lapped. They were etched to a convenient thickness by concentrated phosphoric acid and given a final wash in dilute hydrochloric acid.

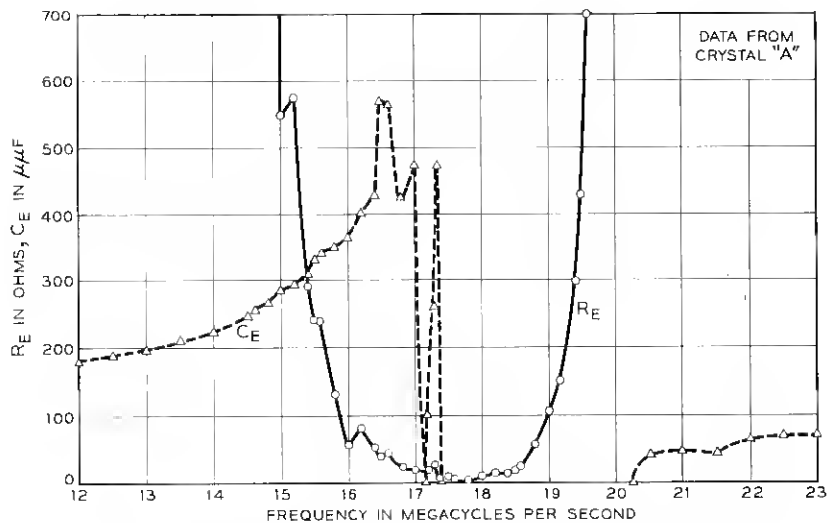


Fig. 3 — Admittance of an unbonded BaTiO<sub>3</sub> single crystal at maximum polarization near its resonant frequency.

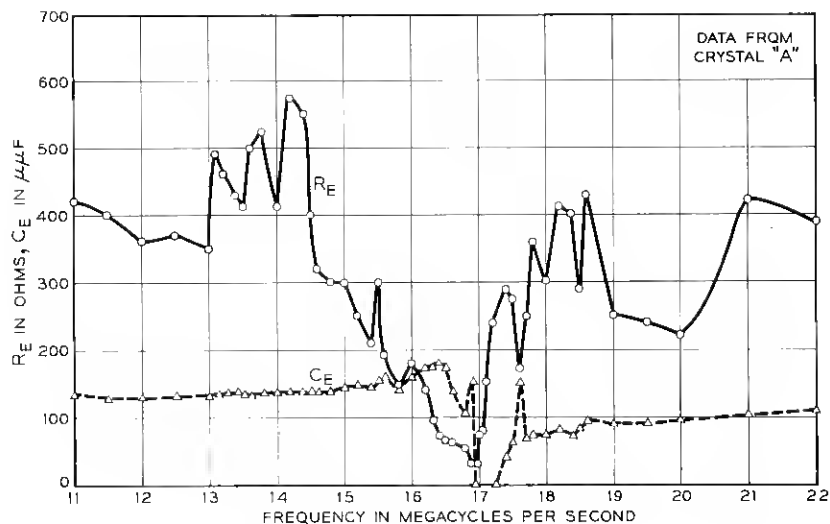


Fig. 4 — Admittance of an unbonded BaTiO<sub>3</sub> single crystal near zero average polarization in the vicinity of its resonant frequency.

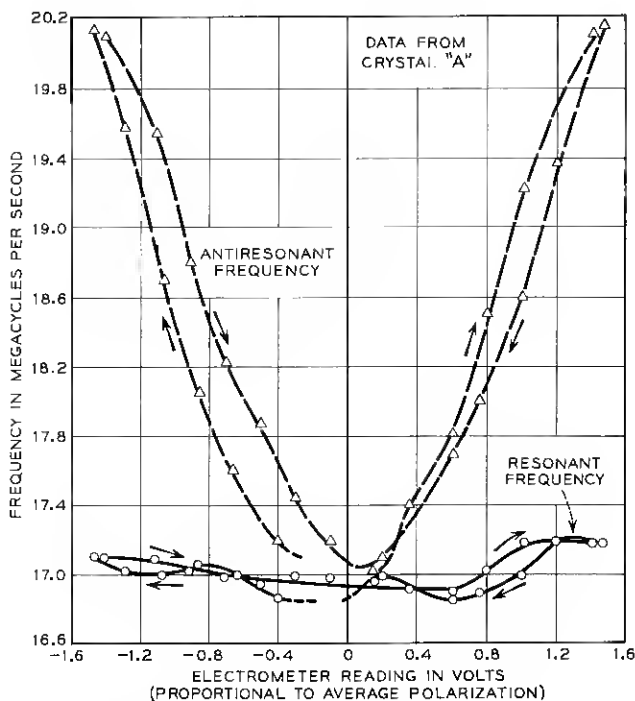


Fig. 5 — Resonant and antiresonant frequencies of an unbonded  $\text{BaTiO}_3$  single crystal plotted vs. its average polarization.

cement to the flat surface of a fused silica rod. This bonded crystal was also used for piezoelectric voltage measurements to be described below. The results of the measurements near resonance on crystal "C" have been plotted as  $C_E(f)$  and  $R_E(f)$  versus frequency in Fig. 6 for the maximum remanent polarization state and in Fig. 7 for the state near zero average polarization. Since  $C_E$  is greater than zero for all frequencies, there were no resonant or antiresonant frequencies for the bonded crystal.

The experimental results in the vicinity of the series resonant frequency may be interpreted by means of equivalent circuits shown on Figs. 2, 6 and 7. The elements of the equivalent circuits consist of  $C_0$ , which depends upon the clamped dielectric constant, and  $R_1$ ,  $C_1$  and  $L_1$  in the series arm. The quantities  $L_1$  and  $C_1$  depend upon the piezoelectric, elastic and dielectric characteristics of the material. In an ideal unloaded piezoelectric resonator,  $R_1$  is zero. A non-zero value of  $R_1$  for a real unbonded crystal is the result of energy being dissipated by the mount-



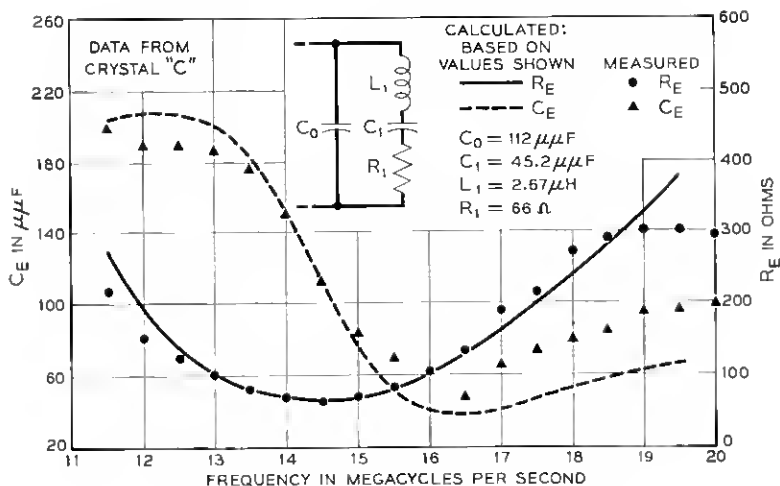


Fig. 6 — Admittance of a bonded BaTiO<sub>3</sub> single crystal at maximum polarization near its resonant frequency.

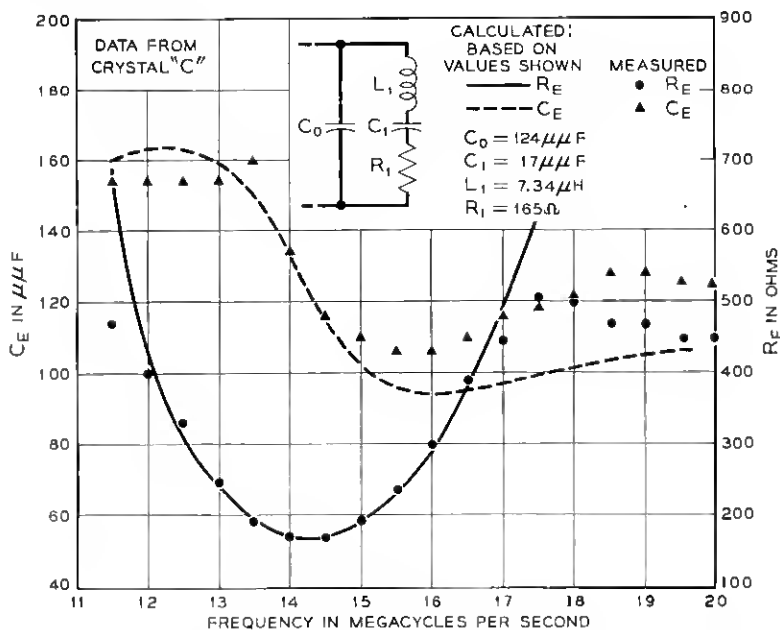


Fig. 7 — Admittance of a bonded BaTiO<sub>3</sub> single crystal near zero average polarization in the vicinity of its resonant frequency.

ing of the crystal or by anelastic mechanisms in the crystal itself. For a bonded crystal,  $R_1$  includes the effects of the loading by the medium to which the crystal is bonded as well as the losses in the crystal itself.

The data in Figs. 3 through 7 indicate that variations in average polarization produce major variations in the admittance of a crystal at frequencies near resonance. These variations are caused in part by variations in the effective clamped dielectric constant, as indicated by  $C_0$ . The relatively large variations are due primarily to changes in the elements in the series arm which depend upon the effective piezoelectric constant and upon loss mechanisms in the crystal. The capacitance ratio\* increases when the polarization approaches zero, indicating that the effective piezoelectric constant is decreasing. The value of  $R_1$  increases as the polarization approaches zero, indicating that more energy is dissipated during each cycle by the crystal.

The variation in effective piezoelectric constant is most clearly revealed by the curves of Fig. 5, which show the variation in resonant and antiresonant frequencies as a function of polarization. When the polarization approaches zero, the separation between the two frequencies decreases. Because the square of the effective piezoelectric coefficient,  $d_{33}$ ,† is proportional to  $f_a - f_r$  or  $\Delta f$ , these data indicate a decrease in  $d_{33}$  as the polarization approaches zero. It is possible for the effective piezoelectric coefficient to become so small that there is neither a resonant nor an antiresonant frequency; i.e., the variation in  $C_E$  is reduced so that it never passes through zero. Fig. 5, in the case when the polarization was varied from positive to negative values, shows gaps in the curves for  $f_r$  and  $f_a$  in the region of zero polarization. These gaps were the result of the disappearance of  $f_r$  and  $f_a$  caused by the near-zero value of  $d_{33}$ .

**2.2.2 Admittance Measurements at Frequencies Removed from Resonance.** The admittance of crystal "A" was measured at 100 kc as a function of average polarization. The results of these measurements are shown in Fig. 8. The 100-kc plot agrees with a similar observation by Drougard and Yonng<sup>3</sup> in that the capacitance of crystals in unsaturated polarization states is lower than that in saturated states. Measurements of admittance were also made above the resonant frequency in the thickness-extensional mode and, in this case, a surprising difference was observed in the variation of capacitance with polarization. Fig. 9 shows the results for admittance measurements made on crystal "B" at 26

\* The capacitance ratio,  $r$ , is defined in terms of elements in the equivalent circuit as  $C_0/C_1$ . The elements  $L_1$  and  $C_1$  are interrelated by the requirement that  $\omega_s^2 = 1/L_1 C_1$ .

† The symbols used for all elastic and electric quantities will be those given by the IRE Standards on Piezoelectric Crystals, 1949, unless otherwise noted.

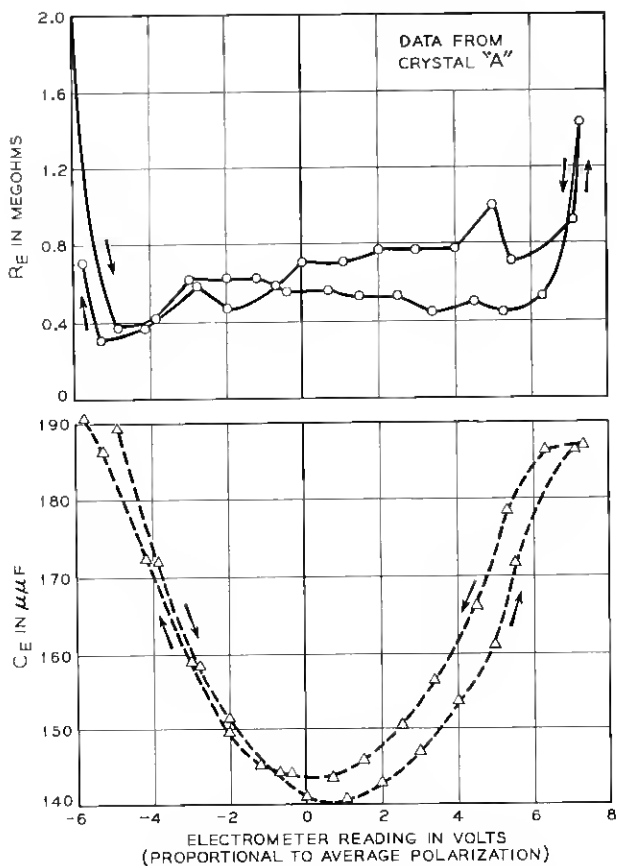


Fig. 8 — Admittance of an unbonded BaTiO<sub>3</sub> single crystal at 100 kc vs. its average polarization.

mc, which is approximately twice the fundamental resonant frequency of this crystal. It can be seen that the dielectric constant for zero polarization is higher than that for maximum polarization.

The data shown in Figs. 8 and 9 are representative of the results obtained on our better crystals for the variation in the small signal dielectric constant as a function of polarization and of frequency. These results will now be summarized and given a qualitative interpretation.

At low frequencies, the capacitance, and hence the dielectric constant, is roughly a parabolic function of polarization, being maximum at the extremes in polarization and having at zero polarization a minimum which is down 10 to 25 per cent from the maximum value. At higher

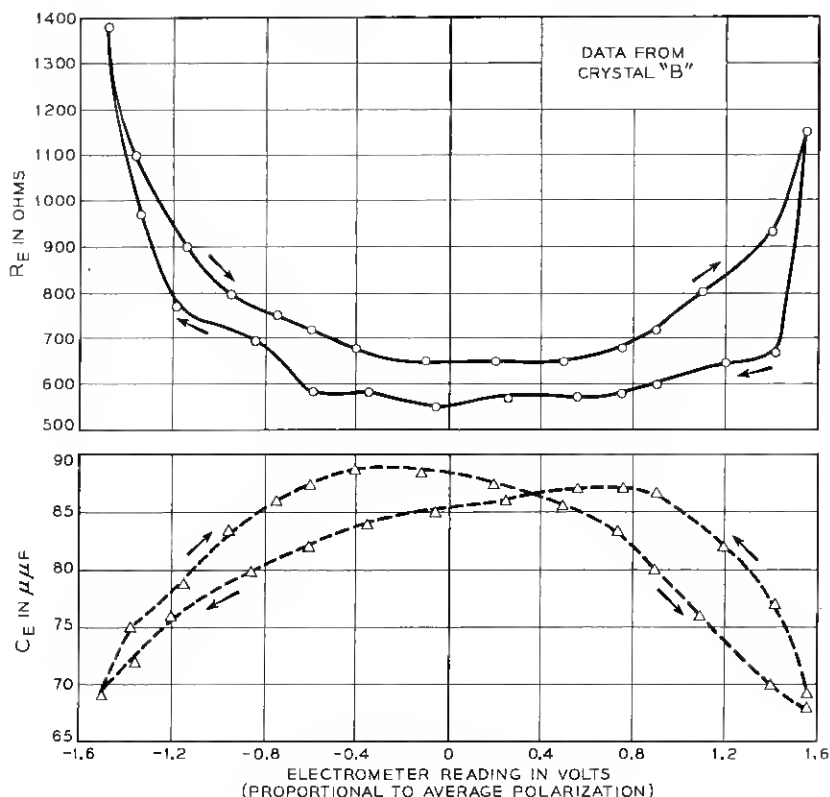


Fig. 9—Admittance of an unbonded  $\text{BaTiO}_3$  single crystal at 26 mc vs. its average polarization.

frequencies, the dielectric constant is again approximately a parabolic function of polarization, but in this case the parabola is turned downward; i.e., the maximum value of the dielectric constant occurs at zero polarization and the minimum values occur at the extremes in polarization. On the high-frequency side of resonance, the minimum values have been observed to be 20 to 30 per cent below the maximum value at zero polarization. Values for dielectric constants calculated for three  $\text{BaTiO}_3$  single crystals are given below. These values have not been corrected for the fringing polarization which was present, since the samples were not fully electroded. The effect of such a correction would be to lower the values of the dielectric constants; consequently, the values given in Table I should be regarded as upper limits on the corrected values.

TABLE I

Crystal	$f_r$ (mc)	$K_{LF,MP}$	$K_{LF,ZP}$	$K_{HF,MP}$	$K_{HF,ZP}$
A	17.18	222	165	94	129
B	12.85	132	111	57	79
C	14.35	169	145	98	122

The symbols used in Table I are defined as follows:

- $K_{LF,MP}$  = low-frequency dielectric constant at maximum polarization,  
 $K_{LF,ZP}$  = low-frequency dielectric constant at zero polarization,  
 $K_{HF,MP}$  = high-frequency dielectric constant at maximum polarization,  
 $K_{HF,ZP}$  = high-frequency dielectric constant at zero polarization.

There is considerable variation in the values of the dielectric constants, and we attribute this to variations in the structures of the individual crystals, but in each case it is true that

$$K_{LF,MP} > K_{LF,ZP} > K_{HF,ZP} > K_{HF,MP}. \quad (2)$$

The polarization dependent behavior observed at low frequencies has received an interpretation by Drougard and Young.<sup>3</sup> They suggest that the decrease in dielectric constant with decreasing polarization is a consequence of the arrangement of many antiparallel domains in the crystal. The extensional strains developed in these domains under the influence of an applied field oppose each other, resulting in a reduction in the magnitude of strain and consequent reduction in the total energy stored in elastic deformation of the crystal. The crystal is taken as "thickness-clamped" at zero polarization and at frequencies below resonance. Drougard and Young did not consider variations in the dielectric constant at high frequencies with variations in polarization.

In order to provide a qualitative explanation for the difference between  $K_{LF,ZP}$  and  $K_{HF,MP}$ , we suggest that the interpretation of Drougard and Young be supplemented by the inclusion of shear strains at the 180° domain walls. When a low-frequency signal is applied to a crystal in the zero polarization state, the total energy stored in strain is less than at maximum polarization. However, the crystal cannot be regarded as completely clamped, because an appreciable amount of energy is being stored both in shear strains ( $S_4$  and  $S_5$ ) as well as in extensional strain ( $S_3$ ). The deformation of a crystal at zero polarization by an applied field is pictured in Fig. 10. When a crystal is measured at high frequencies and maximum polarization, the energy stored in strain is least, because the

amplitude of extensional strain is low and no shear strains are present. While the pictured mechanism may account for the difference between  $K_{LF,ZP}$  and  $K_{HF,MP}$ , it does not explain why  $K_{HF,ZP}$  was observed to be greater than  $K_{HF,MP}$ .

In the present work, the fact that both  $K_{HF,ZP}$  and  $K_{HF,MP}$  are considerably lower than  $K_{LF,ZP}$  shows that a crystal is not very well clamped at low frequencies and zero polarization. For a given crystal,  $K_{HF,MP}$  appears to be the best estimate one can make of the clamped dielectric constant, and even it is subject to some doubt. For instance, since the capacitance appears to be still rising with frequency in this range, as can be seen from Fig. 3, the clamped dielectric constant may be higher than  $K_{HF,MP}$ . On the other hand, since transducers mounted on ultrasonic delay lines can generate mechanical vibrations at these same frequencies, the crystal cannot be completely clamped. Consequently,  $K_{HF,MP}$  may be higher than the truly clamped dielectric constant. Finally, since the values of the four dielectric constants varied so much from one crystal to another, it is clear that the crystals used do not provide a good basis for determining the numerical values of the constants.

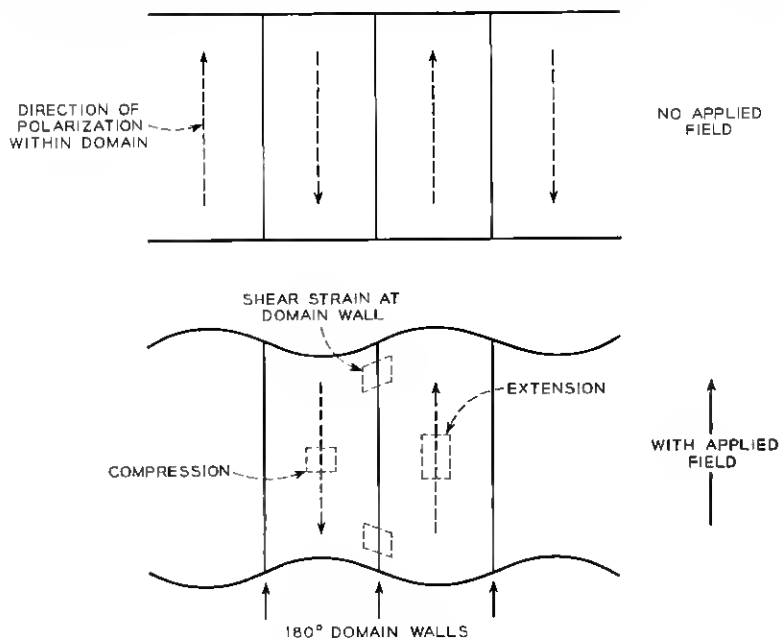


Fig. 10 — Diagram of the deformations produced in a BaTiO<sub>3</sub> single crystal near zero average polarization by a small applied field.

Before leaving the subject of admittance measurements, we should observe two other noteworthy features of the data. First, the crystals dissipate more energy per cycle in the zero polarization state than in the state of maximum polarization. This statement is based on the observation that, away from resonance,  $R_E$  is always lower for zero polarization than for maximum polarization. (See, for example, Figs. 8 and 9.) Bond, Mason and McSkimin<sup>1</sup> have reported that the material is mechanically more lossy in the zero polarization state. They attributed this extra loss to a microhysteresis effect.

The second observation to be made regards the multiple-valuedness of many of the quantities measured as functions of polarization. The data of Figs. 5, 8 and 9 indicate that the components of the admittance measured as functions of polarization have different values well outside the limits of experimental error, although the curve for any quantity retains the same general shape. This scatter probably indicates that the measured values of these quantities are sensitive to the strain condition of the crystal which, in turn, is dependent upon the exact shape and position of the microscopic domains.

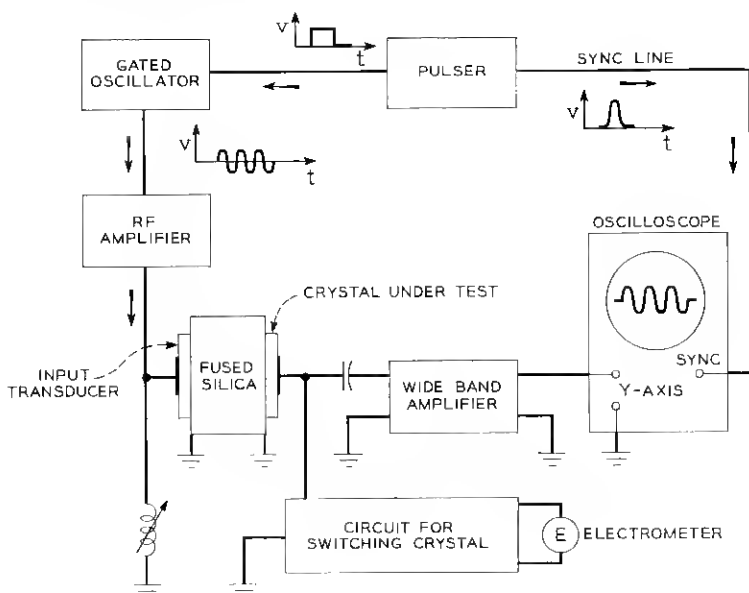


Fig. 11 — Block diagram of apparatus for measuring piezoelectric output voltage of a BaTiO<sub>3</sub> single crystal as a function of its average polarization.

## III. MEASUREMENTS OF PIEZOELECTRIC VOLTAGE GENERATED BY ULTRASONIC EXCITATION

Two  $\text{BaTiO}_3$  single crystals were bonded with Araldite to the ends of a fused silica rod, forming an ultrasonic delay line. One of the crystals, crystal "C", was used as the output transducer and its piezoelectric output voltage was measured as a function of its average polarization.

The essentials of the experimental arrangement are shown in Fig. 11. A recurrent RF pulse of constant amplitude and frequency excited the input crystal transducer. The elastic dilatational wave traveled the length of the line and excited a piezoelectric response in the output crystal transducer, which was observed on the oscilloscope. The average polarization of the output transducer was set and measured by the circuit of Fig. 1(a).

Fig. 12 shows the dependence of piezoelectric output voltage on average polarization for crystal "C". Other crystals were measured and the shapes of the resulting curves are similar. The shape of the curve for crystal "C" was found to be very insensitive to changes in the frequency or amplitude of the applied mechanical wave. The decreased slope at the ends of the curve in Fig. 12 is due to the increase in capacitance of the crystal at maximum polarization. However, the capacitance variation does not account for the hysteresis of the curve. Almost all the crystals measured showed this same type of hysteresis dependence of piezoelectric voltage on average polarization.

The vertical jumps near zero piezoelectric output voltage were not found for all crystals. On one crystal there was a vertical jump in traversing zero in one direction but not in the opposite direction. When the piezoelectric output signal was displayed on an oscilloscope and observed very carefully, the waveform of the piezoelectric pulse could be seen to vary in time near zero polarization and a distinct minimum amplitude could be moved through the time of the pulse by passing charge slowly through the crystal. The data used for plotting the curve were always the maximum amplitude of the pulse during its entire duration, and the meaning of vertical jumps is just that this maximum never passed through zero.

It is possible to interpret these experimental results in terms of the domain picture of  $\text{BaTiO}_3$  crystals. The simple domain picture of polarization would predict a linear dependence of piezoelectric voltage on average polarization. This can be seen as follows. If the crystal consists of many domains polarized in either of the two directions perpendicular to the electrodes on the large surface of the plate, and if the polarization



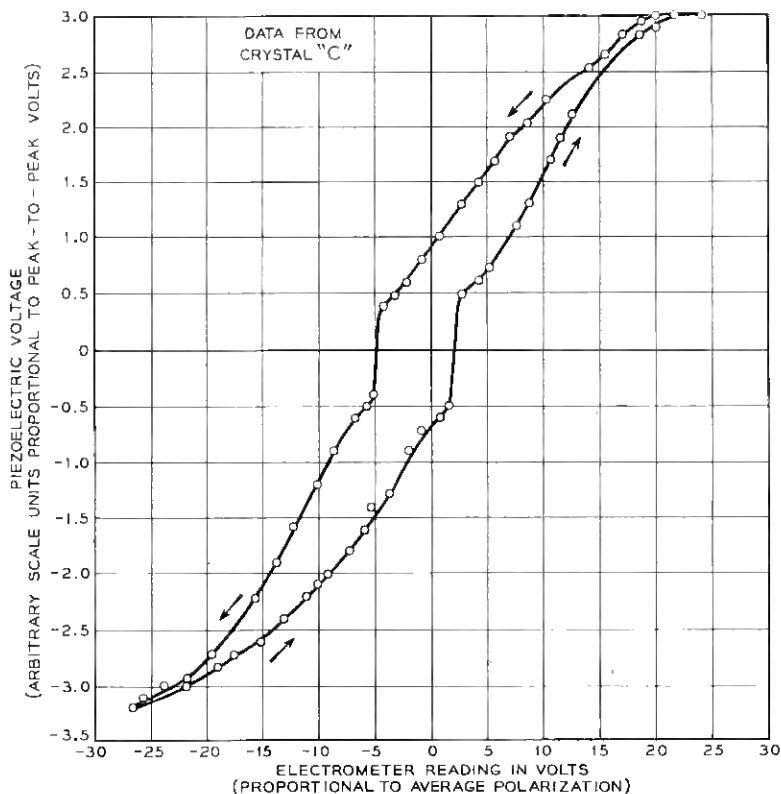


Fig. 12 — Piezoelectric output voltage vs. average polarization of a  $\text{BaTiO}_3$  single crystal subjected to constant amplitude strain waves.

per unit volume within each domain has the same value,  $p$ , then the average polarization is

$$P = \frac{1}{V_c} \int_{V_c} p n dV = p \frac{V_+ - V_-}{V_c}, \quad (3)$$

where  $V_c$  is the volume of the crystal between the electrodes,  $V_+$  and  $V_-$  are the volumes of domains polarized positively and negatively respectively,  $n$  is a unit vector perpendicular to the electrode and  $p = |p|$ . The average polarization is indicated in the experiment as

$$P = \frac{C_2 V_{\text{electrometer}}}{A}, \quad (4)$$

where  $A$  is the electrode area.

Thus we have

$$V_{\text{elec}} = \frac{pA}{C_2} \frac{V_+ - V_-}{V_c}. \quad (5)$$

We assume that  $p$  is a function only of the temperature,  $T$ , and the average strain,  $S = (L - L_0)/L_0$ , where  $L$  and  $L_0$  are the instantaneous and average thicknesses of the crystal. Thus, the piezoelectric voltage is assumed to be due to the change in polarization accompanying a strain, as

$$V_{\text{piezo}} = \frac{A}{C_x} \frac{\partial P}{\partial S} \Delta S = \frac{A}{C_x} \frac{\partial p}{\partial S} \Delta S \frac{V_+ - V_-}{V_c}, \quad (6)$$

where  $C_x$  is the capacitance of the crystal plus the input capacitance of the voltage measuring circuit.

Thus one obtains

$$\begin{aligned} \frac{V_{\text{piezo}}}{V_{\text{elec}}} &= \frac{\frac{A}{C_x} \frac{\partial p}{\partial S} \Delta S \frac{V_+ - V_-}{V_c}}{\frac{pA}{C_2} \frac{V_+ - V_-}{V_c}} \\ &= \frac{C_2}{pC_x} \frac{\partial p}{\partial S} \Delta S. \end{aligned} \quad (7)$$

For constant strain and temperature, all the factors in this last relation, with the exception of  $C_x$ , are constant, independent of average polarization;  $C_x$  is a slowly varying function of average polarization. Thus, we would expect the piezoelectric voltage to be proportional to the average polarization. As Fig. 12 shows, this is not entirely true.

According to the simple picture just presented, we would expect the piezoelectric voltage for maximum positive average polarization to equal that for maximum negative polarization. This was true for some crystals, including the one measured for Fig. 12, but was not true for many others. A plausible cause of this inequality is that some domains are stuck, and are not switched even when the crystal is saturated. That is,  $V_+$ , for example, might never be zero, thus reducing the maximum piezoelectric voltage for negative polarization. These stuck domains would also reduce the switching charge of the crystal from its maximum value. In fact, it was found that all crystals whose positive and negative piezoelectric voltages were very unequal did not switch as much charge as they had switched shortly after plating.

As a final observation, it should be noted that, although the simple

dipole theory leads one to expect a linear relationship between piezoelectric voltage and polarization, what is usually observed is the open-loop type of curve shown in Fig. 12. Upon repeating the polarization cycle in measuring a given crystal, one finds that the individual points are duplicated almost exactly. In this case there seems to be a true hysteresis, as contrasted to the results obtained for admittance measurements as functions of polarization.

#### IV. CONCLUSIONS

The dielectric and piezoelectric constants of *c*-domain BaTiO<sub>3</sub> single-crystal plates are sensitive functions of their average polarization when determined from capacitance measurements using ac voltages much smaller than the coercive voltage. It has been reported<sup>3</sup> that the dielectric constant at frequencies below thickness resonance has a minimum at zero polarization, and our measurements confirm this result. On the other hand, at frequencies above the fundamental thickness-resonant frequency, the dielectric constant has a distinct maximum at zero polarization. The dielectric constant varies about 25 per cent from minimum to maximum in both frequency ranges. In both ranges, the conductance is maximum at zero polarization.

The dielectric constant of BaTiO<sub>3</sub> at high frequencies and maximum polarization is significantly lower than the dielectric constant at zero polarization and low frequencies. This difference indicates that, at low frequencies and zero polarization, the crystal cannot be regarded as completely clamped, and for this reason the dielectric constant at high frequencies and maximum polarization represents a better value to use for the effective dielectric constant at constant strain.

The piezoelectric output voltage of a BaTiO<sub>3</sub> single crystal subjected to constant-amplitude recurrent strain pulses has been measured and found to be approximately proportional to its average polarization. However, departures from linearity were observed. When piezoelectric output voltage was plotted as the ordinate and polarization as the abscissa, a hysteresis dependence was observed. In addition, it was found that the curve of piezoelectric output voltage showed vertical jumps in the vicinity of zero polarization.

The measurements presented in this paper indicate that plate-shaped BaTiO<sub>3</sub> single crystals have a significantly lower dielectric constant and a smaller capacitance ratio when used as resonators in the thickness-extensional mode than do similar resonators made from BaTiO<sub>3</sub> ceramic. These characteristics of the single crystal can be used to advantage in

certain applications such as electromechanical transducers for operation at high frequencies.

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